



Pd/Fe₃O₄ nano-catalysts for selective dehalogenation in wastewater treatment processes—Influence of water constituents

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ABSTRACT

Palladium catalysts can be used for the *selective* removal of halogenated organic compounds from aqueous waste via hydrodehalogenation reactions in the presence of other omnipresent constituents of industrial wastewaters. This detoxification of the water and drastic lowering of the AOX value (adsorbable organically bound halogens) can prevent the need for further cost-intensive treatment or discharge into waste incineration plants. Often, the water can then be released to municipal sewage plants.

The present paper deals with a highly active, magnetically re-extractable nanoscale Pd-on-magnetite catalyst (Pd/Fe₃O₄) which has been developed for application in wastewater treatment processes. The study provides insight into the performance of this catalyst and gives information about its general applicability under wastewater conditions and its sensitivity towards constituents of a wastewater matrix.

The catalyst can tolerate various inorganic and organic substances in relevant concentrations. Wastewaters containing a high background concentration of organic solvents can also be cleaned from halogenated pollutants. However, waters which contain heavy metals such as lead or mercury or reduced sulphur species such as sulphides need specific pre-treatments prior to Pd-catalysed hydrodehalogenation.

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1. Introduction

Palladium catalysts bear a high potential for an efficient hydrodehalogenation of water pollutants, as has been shown in many laboratory studies [1–3]. Their utilization for treatment of contaminated groundwater has been demonstrated at several sites [4–8]. In the chemical or environmental industries, Pd already plays a significant role as a component of catalysts for fine chemical syntheses [9], hydrogenation reactions [10] or in catalytic converters in the automotive industry [11,12]. However, to the best of our knowledge, it has not yet been employed in wastewater treatment concepts. In particular for industrial wastewaters containing chlorohydrocarbons (CHCs), Pd could provide the option of their *selective* removal without involving other water constituents such as non-halogenated solvents. This would render costly non-selective adsorptive or oxidative water treatment processes unnecessary, including the energy-consuming incineration.

With the focus on applicability of Pd catalysts for wastewater treatment, we recently described a novel magnetically recoverable Pd/Fe₃O₄ nano-catalyst ($d_{\text{particle}} = 20\text{--}30\text{ nm}$) [13] showing an

extremely high hydrodechlorination (HDC) activity and offering the possibility of an efficient particle removal from the treated water via magnetic separation. This – for the first time – opens up the utilization of the Pd-based catalyst for commercial use in wastewater treatment.

It is well known that Pd catalysts are sensitive against a number of chemical species, such as heavy metals or reduced sulphur compounds [14–16]. Industrial wastewaters containing such substances are either not treatable with Pd-containing catalysts or they have to be pre-treated by appropriate procedures [3]. In contrast to irreversible poisoning, there are also catalyst deactivation phenomena which may be temporary or may be avoided by adequate process control such as high water turbulence. These phenomena are typically caused, e.g., by Pd surface blockage due to adsorption of substances such as minerals, salt precipitations, accumulation of debris, inorganic oxides, biofilms, organic co-adsorbates or natural organic matter (NOM) [14,17–21]. Carbon monoxide was also found to play a role as catalyst poison when applying formic acid as alternative hydrogen source in water. HDC activity is completely inhibited by trace levels of CO [22].

In the special case of nano-catalysts, some additional deactivation phenomena have to be considered which are caused by changes of the particle size or size distribution. Durand et al. described a loss of catalytic activity of Pd nanoparticles (NPs)

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induced by Ostwald ripening—a phenomenon where smaller NPs continue to shrink or dissolve and larger NPs continue to grow [23]. Agglomeration of catalyst particles, crystallite growth and sintering phenomena are further causes for significant loss of activity [14]. For Pd supported on zero-valent iron, Pd dislodgement and formation of iron oxides on the active sites have been described [19]. Apparently, the choice of catalyst support plays an important role for the overall performance of the catalytic system. The ferrimagnetic iron oxide magnetite (Fe_3O_4) has proved its suitability under the desired reaction conditions for wastewater treatment [13].

Some efforts have been already made to protect the Pd catalysts from deactivation by means of applying hydrophobic coatings or supports [24,25]. This strategy has recently been extended to a combination of hydrophobic protection and oxidative pre-treatment of the water with KMnO_4 [3].

For industrial wastewater and process water we consider it an advantage that in general the water components and matrix conditions are known and predictable. Biological processes can mostly be excluded in the initial cleaning stage—a clear simplification compared to groundwater treatment under long-term conditions. In order to predict the behaviour of the Pd catalyst under various wastewater conditions, the present paper provides a systematic study of the performance of Pd/ Fe_3O_4 in the presence of a variety of cations, anions and organic substances common as wastewater constituents. This knowledge will form a basis for optimisation of the catalysts, for their efficient protection and for the development of a Pd-based wastewater treatment technology.

2. Experimental

2.1. Chemicals

All reagents and CHCs were purchased in the highest grade available from Merck (Germany) or Sigma–Aldrich (Germany) and used as received. Pd/ Fe_3O_4 NPs were prepared using commercially available magnetite NPs ($d = 20\text{--}30\text{ nm}$; Aldrich, Germany). 15 g of magnetite was suspended in 2 L of deionized water, treated for 10 min in an ultrasonic bath and then spiked with 22.5 mg Pd originating from a Pd stock solution ($\text{Pd}(\text{ac})_2$ in THF). The mixture was vigorously shaken, whereby decolourisation of the orange supernatant (visible after magnetic separation of the magnetite particles) indicated the Pd uptake by the magnetite nanoparticles. Subsequent H_2 purging of the suspension for 1 h ensured complete reduction to Pd^0 . The catalyst was washed with deionized water and dried in vacuum. The palladium content of 0.15 wt% Pd, determined by X-ray fluorescence measurements, corresponds to a complete uptake of the applied Pd salt by the carrier. CO-chemisorption measurements (BELCAT catalyst analyser, BELCAT-B, BEL Japan, Inc.) indicate maximum dispersion of the Pd ($D_{\text{Pd}} \approx 1$). A more detailed particle characterization is described elsewhere [13]. For reasons of comparison, Pd/ Al_2O_3 was used in some experiments (0.5 wt% Pd on $\gamma\text{-Al}_2\text{O}_3$ as eggshell catalyst; further data are to be found in [3]).

2.2. Batch reactor

The performance of the Pd/ Fe_3O_4 nano-catalyst in HDC reactions was studied in batch experiments using chloroform (CF) and trichloroethylene (TCE) as probe compounds. 250-mL clear screw-cap bottles equipped with Mininert[®] valves were used with 200 mL reaction solution. The catalysts were preconditioned by purging the suspension with H_2 for 30 min and treating in an ultrasonic bath for about 10 min prior to use in HDC tests. The catalyst concentration was adjusted to the reaction rates in such a way that a sufficient number of sampling points (≥ 5) could be

obtained over the course of reaction. The headspace over the suspension (50 mL) was pure H_2 , forming a sufficient reservoir of reductant. Most reactions were started by adding a methanolic CHC stock solution; some reactions were initiated by adding the preconditioned catalyst as aqueous suspension, in both cases carefully excluding air. The bottle was then continuously shaken on a horizontal shaker (210 rpm) throughout the experiment. The reaction kinetics was monitored by means of headspace analysis of educts and products (25 μL gastight glass syringe) using a GC–MS device (QP 2010, Shimadzu Corp., equipped with a 25 m DB1 capillary column). Evaluation of the catalyst performance was carried out using the specific catalyst activity $A_{\text{Pd},i}$ for the HDC of the CHC i according to Eq. (1) [7]:

$$A_{\text{Pd}} = \frac{1}{c_{\text{Pd}}\tau_{1/2}} = \frac{\ln(c_{t1}/c_{t2})}{\ln 2 c_{\text{Pd}}(t_2 - t_1)} \quad \text{in } [\text{L g}^{-1} \text{ min}^{-1}] \quad (1)$$

where c_{Pd} is the Pd concentration, $\tau_{1/2}$ is the CHC's half-life (obtained from its disappearance kinetics), t_1 and t_2 are two arbitrarily chosen sampling times, and c_{t1} and c_{t2} are the corresponding CHC concentrations. The specific catalyst activities $A_{\text{Pd},i}$ were calculated either from the CHC conversion data or from those of product formation. The second approach was preferably used for low degrees of conversion for reasons of accuracy, and *vice versa* the CHC disappearance for high conversion degrees. The value of $A_{\text{Pd},i}$ is equivalent to a second-order rate coefficient and can be transformed into a first-order rate coefficient k_{obs} [s^{-1}] regarding CHC disappearance according to $k_{\text{obs}} = \ln 2 \cdot A_{\text{Pd},i} \cdot c_{\text{Pd}}$ or alternatively into a turnover frequency according to TOF [s^{-1}] = $\ln 2 \cdot A_{\text{Pd},i} \cdot 106 [\text{g mol}^{-1}] \cdot c_{0,i} [\text{mol L}^{-1}] / D_{\text{Pd}}$, where $c_{0,i}$ is the initial concentration of the CHC.

2.3. Studies of matrix effects

The influence of matrix constituents on the HDC performance of the Pd/ Fe_3O_4 catalyst was studied in batch experiments using the experimental setup described above. In most experiments, the pH value of the reaction media was maintained at neutral or slightly basic conditions (in order to avoid catalyst dissolution and pronounced particle agglomeration) and, if necessary, buffered with 5 mM Na_2SO_4 /5 mM NaHCO_3 ($\text{pH} \approx 8.5$, $\kappa \approx 780 \mu\text{S cm}^{-1}$). In some experiments, the pH value of the reaction medium had to be adjusted using HCl (e.g., pH 5.5 required for keeping some metal ions in the dissolved state). For acidic start conditions, buffers were not applied because of only marginal pH changes by HCl generation.

For studies of the catalyst pH dependence, the pH values of reaction solutions were adjusted by addition of HCl or NaOH. The zeta potentials of the catalyst were measured by means of the dynamic light scattering technique (Zetasizer Nano ZS, Malvern Instruments, $c_{\text{particle}} = 100 \text{ mg L}^{-1}$ suspended in 1 mM NaCl). Commonly, deionized water (referred to as pure water, $\kappa \approx 1 \mu\text{S cm}^{-1}$) was used to prepare the reaction media containing the various salts and other added water constituents simulating industrial wastewater.

After preconditioning of the catalyst (25–65 mg L^{-1} Pd/ Fe_3O_4 , corresponding to $c_{\text{Pd}} = 40\text{--}100 \mu\text{g L}^{-1}$) the reaction was started by adding the CHCs as a methanolic stock solution. Methanol has no influence on the catalyst performance in the applied concentrations. The ionic matrix components were added as aqueous solutions into the running experiments, carefully excluding air. The analysis of the HDC probe substances was carried out via headspace sampling as described above.

Dissolved metal ions were analysed by means of inductively coupled plasma mass spectrometry (ICPMS) with electrothermal vaporization using a PerkinElmer Sciex ELAN 5000 ICPMS. The

sample introduction by electrothermal vaporization was performed with a HGA-600MS system (PerkinElmer). Anions were measured by means of ion chromatography (Dionex IC25 with ionpak AS15 column).

2.4. Continuous flow reactor

The continuous flow experiments were carried out using a 2.5 m long coiled glass tube ($d_{\text{inner}} = 3.3$ mm, $V_R = 21.2$ mL). Chlorobenzene (MCB) was used in these experiments as probe compound. The reactor was fed with MCB-containing, hydrogen-saturated water ($C_{\text{MCB}} = 20$ ppm = 0.18 mM, $C_{\text{H}_2} = 0.8$ ppm = 0.4 mM) which was pumped with a volumetric flow rate of $V = 4.7$ mL min⁻¹ (piston pump, ISMATEC MCP). The contaminated water was supplied from a glass storage vessel ($V = 2$ L) with a gastight screw-on two-fold port, one port connected to a pressure-equalization flask and the second to the pump. The 50 mL pressure-equalization flask (filled with 20 mL water slowly purged with hydrogen) was connected to the storage vessel by flexible PTFE tubing. This ensured the replacement of the volume of withdrawn contaminated water by hydrogen, and the exclusion of air admission. From the second port the contaminated water was pumped into the reactor. 10 cm from the reactor coil inlet, a sampling port with a Luer Lock adapter was installed for liquid sampling (MCB start concentration). A second inlet port (2 cm in flow direction from the first) was fed by a smaller piston pump (ISMATEC, ceramic pump head) with the catalyst as aqueous suspension. The catalyst (125 mg) was added to a glass flask, dispersed in 500 mL deionized water. This particle stock suspension was treated in an ultrasonic bath for 60 min prior to use, then continuously stirred and purged with hydrogen while part of the suspension was pumped through a 15 cm long PTFE tubing ($V = 5.3$ mL min⁻¹) into the reactor. The residence time of the water in the reactor coil was $\tau_{\text{reactor}} = 2$ min. At the reactor outlet, a second sampling port was installed for taking liquid samples of the reaction suspension. The liquid samples (1 mL) were filled in small vials (2 mL). Further dechlorination within the vials was prevented by the addition of Na₂S. The 1 mL reaction suspension and the headspace in the vial were equilibrated by vigorous shaking (1 min) and a 25 μ L gas sample was taken from the headspace for analysis using GC–MS.

2.5. Catalyst extraction

The Pd/Fe₃O₄ NPs can be easily separated from suspensions at the laboratory scale using strong permanent magnets (NdFeB magnets with a remanence of 1.3 T; Supermagnete Webcraft GmbH, Switzerland). For larger water volumes, the enhanced magnetic separation technique described by Hoffmann and Franzreb has been applied [26]. As laboratory scale magnetic separator, a small glass vessel was utilized which was filled with stainless steel wool. This was attached to the outlet of the continuous flow reactor and placed in a magnetic field generated by a permanent magnet. The NPs were magnetically collected and precipitated on the steel wool inside the vessel.

3. Results and discussion

In order to evaluate the catalyst performance and its applicability for treatment of industrial wastewaters, water samples of various composition and origin were used as HDC reaction medium. Unprotected nanoparticulate Pd/Fe₃O₄ served as HDC catalyst in discontinuous batch reactions and continuous flow-through studies using a coiled reactor tube. For TCE reduction, an extremely high reaction rate can be reached under ideal conditions (second-order rate coefficient $k_{\text{TCE}} = 1.6 \times 10^4$ L g⁻¹ min⁻¹ or specific Pd activity $A_{\text{Pd,TCE}} = 2.3 \times 10^4$ L g⁻¹ min⁻¹ [13]). Therefore, TCE served as probe CHC for the study of instantaneous matrix

effects on the catalyst performance. In comparison to TCE, CF reacts markedly slower in HDC reactions [17], therefore it was used for the observation of long-term effects.

3.1. HDC in pure water

The influence of trace level water constituents on the catalyst performance was studied with ultra-pure water (laboratory water purifier Millipore® Simplicity 185, $\kappa \approx 0.055$ μ S cm⁻¹), pure water (deionized water, $\kappa \approx 1$ μ S cm⁻¹, originating from an in-house supply ion-exchange unit, Millipore® ELIX35 with two storage tanks and a water circulation line system) and tap water (local domestic water supply of drinking water, $\kappa \approx 600$ μ S cm⁻¹). As reported previously, for TCE a two-step kinetics was observed in pure and ultra-pure water where the catalytic activity $A_{\text{Pd,TCE}}$ raised from the initial value of $A_{\text{Pd,TCE,A}} = 6100 \pm 560$ to $A_{\text{Pd,TCE,B}} = 22500 \pm 1700$ L g⁻¹ min⁻¹ [13]. The initial catalyst activity at $C_{0,\text{TCE}} = 0.076$ mM corresponds to TOF = 0.6 s⁻¹, which can be considered as a very high value. Fig. 1 shows such typical reaction kinetics of TCE which follows in the first step a first-order kinetics up to a conversion degree of about 90%. After this, the reaction rate increases independently of the initial TCE concentration (1 or 10 ppm) and reaches in the second step extremely high values [13]. In contrast to the above, in the case of tap water continuous first-order kinetics was reproducibly observed up to high conversion degrees (>6 half-lives, see Fig. 1). However, the catalyst activity was decreased by almost one order of magnitude ($A_{\text{Pd,TCE}} = 700$ L g⁻¹ min⁻¹). Two reaction modes were carried out: (i) the catalyst was pre-treated in tap water and the reaction started by adding TCE (depicted in Fig. 1); (ii) the catalyst was preconditioned in pure water and then added to the reaction medium tap water. Also in the latter case, within the first few minutes of TCE dechlorination, a significant activity decrease to activity values of around 700 L g⁻¹ min⁻¹ was observed. Thus, one or more constituents of potable tap water have a significant influence not only on the continuity of the reaction kinetics but also especially an instantaneous effect on the reaction rate. Since the causes of these effects were not clear, several compound classes came into consideration for being tested.

The much slower HDC of CF was also studied in the three different water systems. The specific catalytic activities in ultra-pure water and pure water are again identical and are in the range of $A_{\text{Pd,CF}} = 140$ L g⁻¹ min⁻¹. In tap water, the specific catalytic activity decreased by a factor of 14 to $A_{\text{Pd,CF}} = 10$ L g⁻¹ min⁻¹. The activity decrease found for TCE was a factor of 9 for $A_{\text{Pd,TCE,A}}$ and a factor of 29 for $A_{\text{Pd,TCE,B}}$. This is in the same order of magnitude. However, for CF the type of reaction kinetics was not influenced by the reaction medium.

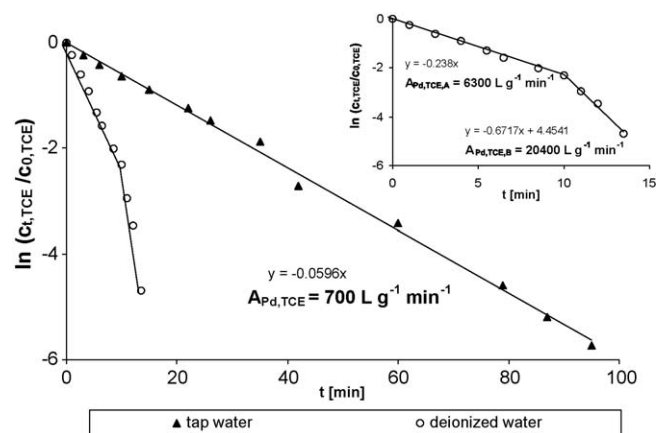


Fig. 1. TCE hydrodechlorination kinetics in deionized and tap water ($C_{0,\text{TCE}} = 1$ mg L⁻¹, $C_{\text{catalyst,deion.}} = 25$ mg L⁻¹, $C_{\text{catalyst,tap}} = 75$ mg L⁻¹).

Since drinking water is one of the most controlled comestible goods and has to fulfill strict purity requirements, a drastic catalyst deactivating effect was not expected. All heavy metals measured via ICPMS (Fe, Cd, Cr, Cu, Mn, Pb, Zn) showed concentrations below their detection limits (typically $<0.03 \text{ mg L}^{-1}$ except for Pb with $c_{\text{Pb}} < 0.1 \text{ mg L}^{-1}$, see Table 2). Water hardness components such as Ca^{2+} and Mg^{2+} were determined with concentrations of $c_{\text{Ca}^{2+}} = 78 \text{ mg L}^{-1}$ and $c_{\text{Mg}^{2+}} = 11 \text{ mg L}^{-1}$. Additionally, some traces of barium ($c_{\text{Ba}^{2+}} = 0.08 \text{ mg L}^{-1}$) were found. This tap water is classified as moderately hard water according to the water supplier and no irregular metal content was found. Although tap water already gave rise to a significant loss of catalyst activity, the measured catalyst activities of $A_{\text{Pd,TCE}} = 700 \text{ L g}^{-1} \text{ min}^{-1}$ and $A_{\text{Pd,CF}} = 10 \text{ L g}^{-1} \text{ min}^{-1}$ are still very high compared to other Pd-containing catalysts such as Pd/ Al_2O_3 in powdered and granular form [1–3].

In ultra-pure water, the typical two-phase reaction kinetics of TCE known from all experiments in pure water was observed. However, the faster second reaction phase $A_{\text{Pd,TCE,B}}$ starts earlier (TCE conversion degree of approximately 40%). This may be explained by the total absence of any disturbing matrix influences, such that the Pd surface can be preconditioned optimally.

For identification of activity-reducing matrix constituents, in a first treatment of the tap water a cation exchange resin (DOWEX-50W, Sigma, 50–100 mesh) was used, followed by neutralization of the water pH value with NaOH. This caused a moderate increase of the catalyst activity ($A_{\text{Pd,TCE}} = 1900\text{--}6600 \text{ L g}^{-1} \text{ min}^{-1}$ and $A_{\text{Pd,CF}} = 24 \text{ L g}^{-1} \text{ min}^{-1}$). Anion exchange was not carried out because typical anions in drinking water (except sulphide and high concentrations of iodide) could be excluded from suspicion as catalyst poisons in the concentrations present (Table 1). After the cation exchange step, the tap water was slowly filtered through a bed of granular activated carbon (GAC, Norit GCN 1240) for removing organic species. GAC particles were carefully removed by filtering the water prior to use as HDC medium ($d_{\text{pore}} = 0.45 \mu\text{m}$). The GAC filtration provided approximately the full catalytic activity known from pure water ($A_{\text{Pd,TCE}} = 8500\text{--}30,000 \text{ L g}^{-1} \text{ min}^{-1}$ and $A_{\text{Pd,CF}} = 90 \text{ L g}^{-1} \text{ min}^{-1}$). Although this indicates organic compounds as catalyst inhibitors, the unspecific sorption potential of activated carbon does not permit distinct conclusions. In order to remove

microorganisms as potential catalyst deactivators, the tap water was autoclaved. However, this did not show any positive effect on the catalyst activity. Since volatile compounds were stripped prior to catalyst testing during hydrogen sparging, the search was focused on non-volatile substances. From the literature it is known that low concentrations of NOM can inhibit Pd-catalysed hydrodehalogenation reactions [20]. Concentrations of NOM in drinking water are normally in the range $\leq 2 \text{ mg L}^{-1}$. Separate batch tests with 5 mg L^{-1} humic acid (Roth, Germany) showed a slow but significant deactivation of the catalyst, typically following a reaction kinetics such as shown in Fig. 2C. Additionally, trace levels (ng L^{-1}) of various organic components, such as bisphenol A, nonylphenols and silicones were detected earlier in the applied tap water [27]. Their concentrations were, however, too low to explain the observed catalyst deactivation effects.

3.2. HDC studies in synthetic wastewater—influence on the reaction kinetics

Industrial wastewaters can have manifold mineral and organic constituents depending on the process they are originating from. Their influence on the HDC performance of Pd/ Fe_3O_4 catalysts was studied using synthetic wastewaters where the suspicious components were spiked to a buffer solution ($5 \text{ mM Na}_2\text{SO}_4 + 5 \text{ mM NaHCO}_3$ in deionized (pure) water, $\text{pH} \approx 8.5$, $\kappa \approx 780 \mu\text{S cm}^{-1}$). This reaction medium with a conductivity close to that of tap water was chosen in order to avoid pH drift during the HDC reaction. The buffer solution itself showed no negative effect on the HDC of TCE. The impact of the various anions and cations on the Pd/ Fe_3O_4 catalyst was studied in a broad concentration range. In addition, the influence of other water constituents such as solvents, selected organic pollutants and natural polymers was evaluated. An overview of the collected data is shown in Tables 1 and 2.

The matrix constituents under study were added such that the concentrations applied in the tests were close to prescriptive discharge limits. We are aware that wastewaters with much higher concentrations of matrix constituents may occur in practice. From the literature strong catalyst poisons such as reduced sulphur compounds or heavy metal ions are known. However, also the

Table 1
Influence of various anions on the catalyst activity, expressed as relative activities ($A_{\text{Pd,TCE,A}}/A_{\text{Pd,TCE,A}}$), measured in a $\text{Na}_2\text{SO}_4/\text{NaHCO}_3$ buffer system adjusted to pH 8.5 (unless stated otherwise) and containing water hardness builders ($c_{0,\text{TCE}} = 10 \text{ mg L}^{-1}$, $c_{\text{catalyst}} = 25$ to 70 mg L^{-1}).

matrix constituent <i>i</i>	$c_{i,\text{tap water}}$ [mg L^{-1}]	Discharge limit c_i [mg L^{-1}]	$c_{i,\text{tested}}$ [mg L^{-1} , if not otherwise specified]	type of TCE HDC kinetics (see figure 2)	$\frac{A_{\text{Pd,TCE,A}}}{A_{\text{Pd,TCE,A}}}$
$\text{Na}_2\text{SO}_4/\text{NaHCO}_3$ standard reaction medium	-	-	5 mM/5 mM	A	1
F^-	0.4	30 ^[38]	95	5 mM	1
Cl^-	40	1000 ^[39]	177		1
Br^-	<0.2	-	400		1
I^-	n.a.	-	635		0.03
NO_3^-	2	30 (N_{total}) ^[38]	310		1
SO_4^{2-}	130	2000 ⁽⁵⁾ [39]/600 ^[39]	480	A	1
HS^- (pH = 10)	n.a.	1 ^[38]	Pd:S = 30:1	C	0.11
HS^- (pH = 10)	n.a.	1 ^[38]	Pd:S = 1:1	C	0.04
HS^- (pH = 10)	n.a.	1 ^[38]	Pd:S = 1:2	D	<0.0001
H_2S (pH = 6)	n.a.	-	Pd:S = 30:1	C	0.16
SO_3^{2-}	n.a.	20 ^[38]	Pd:S = 1:1	A	1
SO_3^{2-}	n.a.	20 ^[38]	Pd:S = 1:5	A	1
SO_3^{2-}	n.a.	20 ^[38]	Pd:S = 1:150	C	0.02
HPO_4^{2-}	0.1	2 ⁽⁵⁾ [38]/50 ^[38] (P_{total})	5	A	1
HPO_4^{2-}	0.1	2 ⁽⁵⁾ [39]/50 ^[39] (P_{total})	50	A	1
MnO_4^-	n.a.	-	0.01 mM	B	0.02/0.43
$\text{NaHCO}_3/\text{CaCl}_2$ ⁽²⁾	n.a. ⁽¹⁾	-	5 mM/5 mM ⁽³⁾	zero order	1
$\text{NaHCO}_3/\text{CaCl}_2/\text{MgCl}_2$ ⁽²⁾	n.a. ⁽¹⁾	-	5 mM/5 mM/5 mM ⁽⁴⁾	zero order	1

n.a., not analysed. (1) Supplier information: 'moderately hard' with $c_{(\text{Ca}+\text{Mg})} = 2.6 \text{ mM}$, $\text{pH} = 7.6$. (2) Reaction kinetics changes to zero-order kinetics after addition of water hardness builders. (3) Water could be referred to as 'hard water'. (4) Water could be referred to as 'very hard water'. (5) For discharge into watercourse.

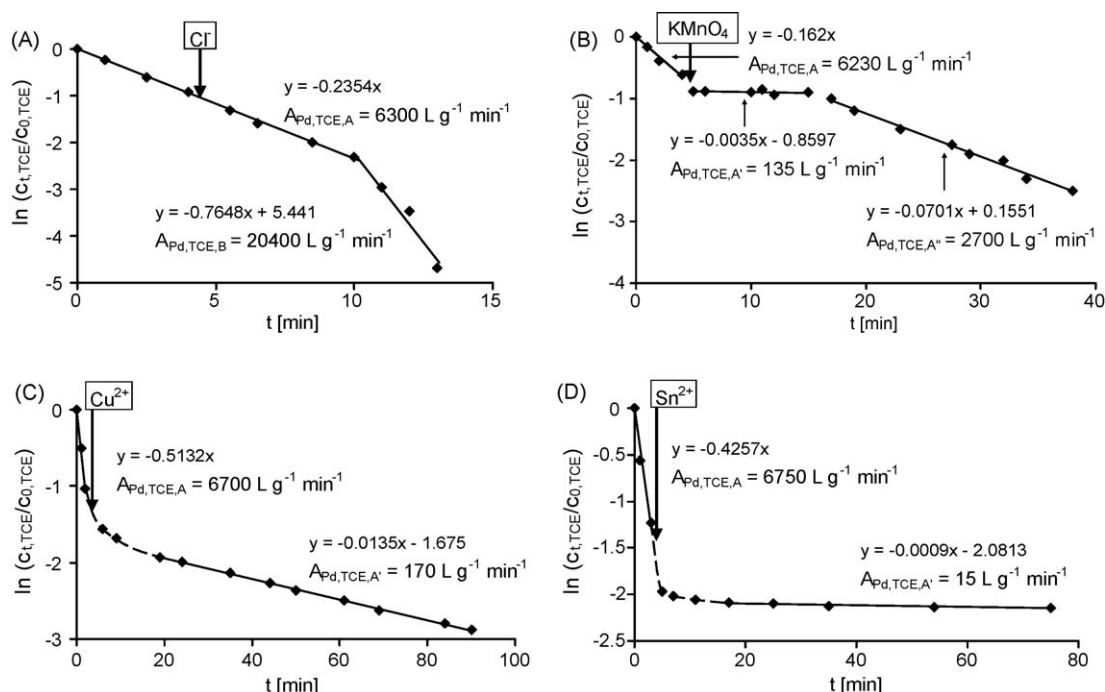


Fig. 2. General types of reaction kinetics found for hydrodechlorination of TCE when adding water pollutants to the reaction suspension – the arrows indicate the addition time ($c_{0,TCE} = 10 \text{ mg L}^{-1}$). (A) Example chloride: kinetics unaffected ($c_{\text{catalyst}} = 35 \text{ mg L}^{-1}$, $c_{\text{Cl}^-} = 177 \text{ mg L}^{-1}$). (B) Example potassium permanganate: temporary deactivation ($c_{\text{catalyst}} = 25 \text{ mg L}^{-1}$, $c_{\text{KMnO}_4} = 0.01 \text{ mM}$). (C) Example Cu^{2+} : partial catalyst deactivation ($c_{\text{catalyst}} = 69 \text{ mg L}^{-1}$, $c_{\text{Cu}^{2+}} = 5 \text{ mg L}^{-1}$). (D) Example Sn^{2+} : poisoned catalyst (incomplete HDC during the extended observation period of 7 days; $c_{\text{catalyst}} = 55 \text{ mg L}^{-1}$, $c_{\text{Sn}^{2+}} = 5 \text{ mg L}^{-1}$).

presence of salts such as chlorides may lead to lower catalyst activities. This was found in gas phase hydrogenation and hydrodechlorination reactions when carried out in less hydrophilic solvent mixtures [28–30].

The water constituents under study were added to the running TCE HDC experiments in such a way that the injections were carried out within the (slower) first reaction phase and after at least three data points within the undisturbed regime had been collected. Fig. 2 shows typical effects on the reaction kinetics. There is either no significant effect on the HDC rate after adding the target contaminant, as found for 5 mM chloride (Fig. 2A), or a negative influence. Fig. 2B shows an initial catalyst deactivation after adding

0.01 mM KMnO_4 followed by an almost complete recovery after a few minutes. Another typical deactivation profile is shown in Fig. 2C for 0.08 mM Cu^{2+} , where the catalyst activity is reduced but stable at a lower level. In Fig. 2D an example of a complete and irreversible catalyst poisoning (0.04 mM of complex tin ions) is given.

Fig. 2 reaction kinetics categories are also listed in Tables 1 and 2. The specific catalytic activities $A_{\text{Pd,TCE,A}}$ and $A_{\text{Pd,TCE,A'}}$ measured before and after addition of the contaminant were compared when following a first-order kinetics as shown in Fig. 2 (continuous lines). The ratio $A_{\text{Pd,TCE,A'}}/A_{\text{Pd,TCE,A}}$ clearly indicates the deactivation impact of the matrix constituent on the HDC rate.

Table 2

Influence of various cations on the catalyst activity, expressed as relative activities ($A_{\text{Pd,TCE,A'}}/A_{\text{Pd,TCE,A}}$), measured in deionized water adjusted to pH 5–5.5 (for metal ions and ammonium) and pH 6.5 for phosphate ($c_{0,TCE} = 10 \text{ mg L}^{-1}$, $c_{\text{catalyst}} = 15\text{--}25 \text{ mg L}^{-1}$).

matrix constituent <i>i</i>	$c_{i,\text{tap water}}$ [mg L ⁻¹]	Discharge limit c_i [mg L ⁻¹]	$c_{i,\text{tested}}$ [mg L ⁻¹]	type of TCE HDC kinetics (see figure 2)	$\frac{A_{\text{Pd,TCE,A'}}}{A_{\text{Pd,TCE,A}}}$
NH_4^+	0.01	30 (N_{total}) ⁵⁾ [38]	100	A	1
Fe^{2+}	total iron <0.02	3 ⁵⁾ [38]	5	A	1
Fe^{2+}			10	A	1
Fe^{3+}			5	A	1
Fe^{3+}			5	A	1
Cu^{2+}	<0.04	0.5 ⁵⁾ [38]	5	C	0.03
Pb^{2+}	<0.1	0.5 ⁵⁾ [38]	0.1	C ⁶⁾	0.24
Pb^{2+}	<0.1	0.5 ⁵⁾ [38]	1	D	0.004
Sn^{2+}	n.a.	2 ⁵⁾ [38]	5	C-D	0.002
Zn^{2+}	<0.04	2 ⁵⁾ [38]	5	A	1
Ni^{2+}	n.a.	1 ⁵⁾ [38]	5	A	1
Al^{3+}	<0.04	3 ⁵⁾ [38]	5	A	1
Ba^{2+}	0.08	5 ⁵⁾ [39]	1	A	1
Ba^{2+}	0.08	5 ⁵⁾ [39]	5	A	1
Hg^{2+}	n.a.	0.05 ⁵⁾ [38]	0.1	C	0.02
Hg^{2+}	n.a.	0.05 ⁵⁾ [38]	1	D	0.003
Mg^{2+}	11	-	350	A	1
K^+	5.7	-	10	A	1

n.a., not analysed. (5) For discharge into watercourse. (6) Clear first-order kinetics directly after Pb^{2+} addition.

A large number of test substances did not show a negative influence on TCE HDC, i.e., the reaction kinetics steadily continued to follow the type A kinetics shown in Fig. 2 including the increase in reaction rate (phase 2). Bromide and iodide were previously described in the literature as strong catalyst deactivators. For example, the TCE HDC using Pd/Al₂O₃ (0.5 wt% Pd) was significantly affected by the presence of 50 mg L⁻¹ bromide (Br: Pd ≈ 1300 on molar basis). Pd/Al₂O₃ lost about 4/5 of the initial Pd activity in the presence of 500 mg L⁻¹ Br⁻. This catalyst seems to be significantly more sensitive to bromide poisoning than Pd/Fe₃O₄ [17]. Moreover, in the case of Pd/Fe₃O₄ even a molar ratio of Br: Pd ≈ 1.3 × 10⁴ did not significantly inhibit the HDC. This indicates the strong influence of the catalyst carrier (or the Pd dispersion) on the deactivation behaviour of Pd catalysts. A similar effect was described for chlorophenol HDC where the activity loss for Pd/C was significantly greater than for Pd/Al₂O₃ under the same reaction conditions [31]. The higher resistance of Pd/Fe₃O₄ towards bromide opens up good perspectives for the applicability of Pd/Fe₃O₄ catalysts in hydrodebromination reactions.

When bromide and iodide ions are present simultaneously, only iodide seems to be the 'culprit'. Hydrodehalogenation of iodinated X-ray contrast media with Pd/Al₂O₃ in the presence of bromide was not negatively affected, whereas the reaction at elevated concentrations of the reaction product iodide is [20]. In our studies the magnetite-supported catalyst showed an effect of type C (Fig. 2) caused by the studied iodide concentrations of 1–5 mM. Full poisoning would be expected at even higher iodide concentrations [17].

A similar kinetics as shown in Fig. 2B was observed for HDC of chlorobenzene with Pd/Al₂O₃ in the presence of permanganate [3]. When KMnO₄ was applied in concentrations above a threshold concentration of about 0.08 mM, the HDC of the probe contaminant was interrupted temporarily. After reduction of the permanganate to trace level concentrations, the HDC reaction restarts and reaches almost initial catalyst activity. Addition of KMnO₄ in a molar ratio of Pd: Mn ≈ 1:30 lead to the expected temporary inhibition of TCE HDC as shown in Fig. 2B.

Type C kinetics as shown for the example of Cu²⁺ addition (Fig. 2) was found for the majority of water constituents added in high concentrations to the reaction medium. Their effect can be understood as a dynamic competition for active catalyst sites rather than their irreversible blockage. Deactivation according to type C kinetics can be tolerable, because the HDC reaction may still proceed at an acceptable rate, depending on the concentration of the inhibitor.

Some strong catalyst poisons such as Sn²⁺, H₂S/HS⁻, Pb²⁺, and Hg²⁺ were also identified for the catalytic system under study (Tables 1 and 2). Immediate and complete deactivation of the catalyst occurred as expected and followed the kinetics shown in Fig. 2D. In all cases the poisoning effect is a matter of concentration and exposed Pd surface. However, concentrations where the inhibition starts are very low. The HDC test reaction utilizing the Pd/Fe₃O₄ catalyst already broke down at c_{Hg²⁺} = 1 mg L⁻¹ (molar ratio of Hg: Pd = 7).

3.3. HDC—influence of various substance classes

Reduced sulphur species are the most common catalyst poisons and can be a major problem in all Pd applications under environmental conditions. Since sulphate is ubiquitous in the environment, microbial sulphate reduction is induced in the presence of reducing agents such as hydrogen [8,25,32–34]. Sulphide (independent of its speciation) has a very high deactivation potential. The stoichiometric addition of Na₂S (S: Pd = 1) already leads to catalyst poisoning, however TCE HDC still reached completion (kinetics type C). The increase in sulphide dosage to S: Pd = 2 resulted in a complete poisoning of the Pd/Fe₃O₄ catalyst (type D kinetics).

Sulphite anions are not commonly known as catalyst poisons. Batch studies using a Pd/Fe⁰ catalyst showed full poisoning in the presence of 2 mM sulphite (S: Pd = 20) [35]. For a Pd/Al₂O₃ a drop in catalyst activity of about two orders in magnitude was found with 87 mg L⁻¹ of sulphite in the eluent [34]. For Pd/Fe₃O₄ up to a molar ratio of S: Pd = 5 we did not observe any significant impact on the catalyst activity. This means, sulphite is not a strong catalyst poison compared to sulphide. Traces of sulphite in the wastewater may be tolerable. However, at higher levels of sulphite (c_{SO₃²⁻} = 0.12 mM, S: Pd = 150) the catalyst was partially deactivated (factor 50, cf. Table 1). The absolute sulphite concentration which is tolerable in the wastewater to be treated may still be low in a batch reactor concept.

Organic sulphur compounds such as thiophenes, mercaptans and dialkylsulphides show a behaviour similar to that of inorganic sulphide [15]. Sulphur in its highest oxidation state in the form of sulphate did not affect the catalyst in the concentration range up to c_{sulphate} = 5 mM. No reduction to potential catalyst poisons occurred. This was also observed for other Pd-catalysed HDC systems [34]. Sulphate as counter-ion in combination with calcium and magnesium cations showed no marked influence on the HDC kinetics of TCE at concentrations commonly found in very hard water.

Other anions such as the anions of nitric, carbonic and phosphoric acids showed remarkably low influence on the catalyst activity at the concentrations tested. This is different from the marked impact of these anions on nanoscale Pd/Fe found by Lim and Zhu [35]. The Pd/Fe₃O₄ system, which is comparable in particle size and Pd content to that described in their paper, was found to be much more resistant.

In many cases industrial wastewaters contain considerable amounts of non-chlorinated solvents such as alcohols. This may change the chemical activity of the target compounds in the reaction medium or even the reaction mechanism. HDC batch tests with TCE were carried out in a mixture of 10% (v/v) methanol and pure water as reaction medium. This solvent concentration had no significant influence on the HDC rate and kinetics. An increase in the methanol fraction to 50% (v/v) led to a decrease in Pd activity by a factor of about 20. Nevertheless, compared to conventional Pd catalysts the measured activity remained high (A_{Pd,TCE,A} = 350 L g⁻¹ min⁻¹ and A_{Pd,TCE,B} = 1400 L g⁻¹ min⁻¹). Remarkably, the reaction kinetics still followed type A shown in Fig. 2, which was only observed in cases of almost undisturbed TCE HDC. Using Pd/Al₂O₃ for HDC of contaminated soil extracts containing various amounts of alcohol extractant showed similar trends [36]. Batch tests with chlorobenzene as probe CHC and Pd/Al₂O₃ as catalyst revealed a drop of 30% of the initial A_{Pd,MCB} in mixtures containing 10% methanol (v/v). Increasing the methanol content to 50% (v/v) led to an activity decrease of about 70% [36]. High loads of organic solvents in wastewaters seem to reduce the specific Pd activity, but Pd/Fe₃O₄ catalysts can still operate satisfactorily when the water content remains sufficiently high (e.g., 50%). Water is known to be essential for fast desorption of chloride from the catalyst surface, in order to prevent chloride poisoning as described for HDC in pure organic solvents or in the gas phase [28,29].

The catalyst activity is affected to a minor degree simply by changing the pH value of the reaction medium. As can be seen from Fig. 3A, the effect is about a factor of 2 between the highest and the lowest activity value in the pH range from 5 to 9. The minimum activity value was found around 6000 L g⁻¹ min⁻¹ at near neutral pH values. Acidic as well as alkaline reaction media allow higher catalyst activities of 11,000–120,00 L g⁻¹ min⁻¹.

The measurement of the zeta potentials revealed a point of zero charge pH_{pzc} ≈ 7 (Fig. 3B). At neutral pH values, the nano-catalyst particles visibly tend to agglomeration. An empirical rule defines that colloidal suspensions with absolute zeta potentials of ζ ≥ 30 mV can be considered as stable suspensions due to strong

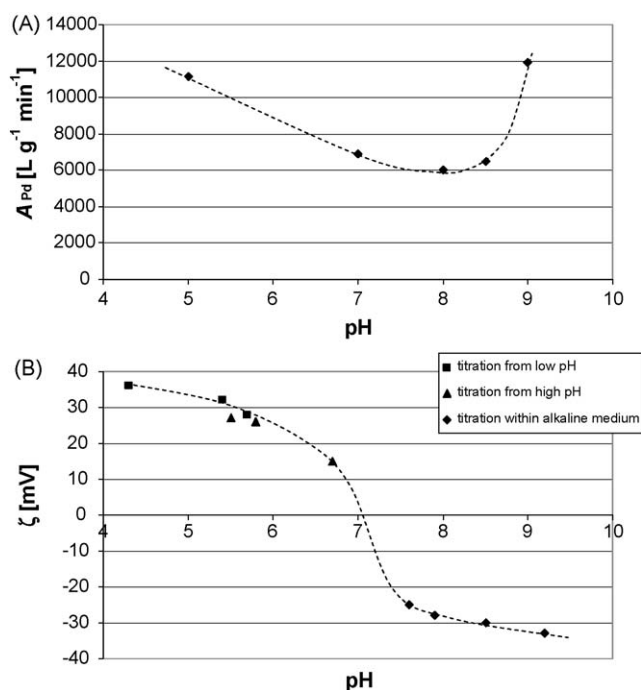


Fig. 3. (A) Dependence of the specific Pd activity on the pH value of the reaction medium and (B) pH dependence of the zeta potential of the Pd/Fe₃O₄ nano-catalyst (always measured after ultrasonic re-dispersion).

repulsion forces between the particles [37]. The slightly higher Pd activity at pH 5 ($\zeta = +35$ mV) and pH 9 ($\zeta = -33$ mV) compared with pH 7–8 can be explained by the higher stability of the catalyst suspension and therefore a higher accessible particle surface area.

Metal cations seem to have very different impacts on the catalyst activity (Table 2). A consistent classification is difficult. Alkali metals and ammonium showed no effects within a broad concentration range, whereas the same applies for earth alkali metals only when no sparingly soluble salts are formed (as would be the case in the presence of carbonates). Water hardeners presumably start to block the Pd surface at concentrations common for 'very hard water' (>3.8 mM total water hardness). Copper and tin tend to deactivate the catalyst at concentrations as low as their discharge limits whereas nickel, zinc, aluminium and manganese (as Mn^{2+} and MnO_4^-) have no negative effect at concentrations permitted in discharge regulations (Table 2). In order to keep all cations in the dissolved state, the pH value was adjusted to between 5 and 6 for these experiments. However, the unbuffered system did not markedly change the pH value during reaction because magnetite can provide some alkalinity. Alkaline zones in the close neighbourhood of the catalyst support may still cause the precipitation of metal hydroxides or oxyhydroxides on the surface. Therefore, it is surprising that the addition of Fe^{2+} and Fe^{3+} ions did not show any deactivation effect on the catalyst. In the literature, deactivation phenomena of Pd/Fe were explained with a reduction in Pd surface due to overgrowing iron oxides originating from the catalyst support [19]. For Pd/Fe₃O₄, the addition of dissolved Fe^{2+} and Fe^{3+} ions as well as potentially leached iron species did not precipitate or form iron oxide coverage on the Pd sites under the reaction conditions chosen. The catalytic activity remained stable after addition of iron salts (up to $10 mg L^{-1} Fe^{2+}$) into a running HDC experiment.

The deactivation by known catalyst poisons such as Pb^{2+} and Hg^{2+} was examined at concentrations lower and higher than the discharge limits (which are set in our region to $c_{Pb^{2+}} = 0.5 mg L^{-1}$ and $c_{Hg^{2+}} = 0.01 mg L^{-1}$). HDC kinetics in the presence of Pb^{2+} showed an interesting effect: although the addition of $1 mg L^{-1}$ of Pb^{2+} led to complete catalyst poisoning (kinetics equivalent to

Fig. 2D), the addition of $0.1 mg L^{-1} Pb^{2+}$ resulted in a clear first-order kinetics where the Pd activity remained surprisingly high ($A_{Pd,TCE,A}/A_{Pd,TCE,A} = 0.24$ for $0.1 mg L^{-1} Pb^{2+}$). Hg^{2+} was found to be more effective in poisoning than Pb^{2+} ($A_{Pd,TCE,A}/A_{Pd,TCE,A} = 0.02$ for $0.1 mg L^{-1} Hg^{2+}$).

Consequently, wastewaters containing catalyst poisons such as sulphide, mercury or lead cannot be efficiently cleaned by Pd catalysts unless an adequate pre-treatment step is carried out or sophisticated measures for catalyst protection are followed [3].

3.4. Future technical implications

The catalyst design was geared to the utilization of the HDC reaction as an efficient treatment method for special industrial wastewaters containing chlorocompounds as problem contaminants. Our goal is the development of a process which is as simple and safe as possible. Since the wastewater types considered can occur continuously or discontinuously in smaller enterprises, two different reactor types were chosen for simulation of the treatment process.

3.4.1. Batch reactor

Pd/Fe₃O₄ nano-catalysts can be effectively used in a batch-wise decentralized treatment of small amounts of wastewaters (in the magnitude of cubic meters) using, e.g., a simple reactor vessel where a magnetic separation unit is installed at the reactor outlet before final water discharge (Fig. 4A). In order to reach a dehalogenation degree of >98%, the residence time of the water in the reactor vessel has to be at least six reaction half-lives ($\tau_R \geq 6\tau_{1/2}$). We see realistic chances of a successful process implementation in small and medium-sized enterprises in the chemical or pharmaceutical industry, where AOX elimination from process waters has to be addressed and where process effluents are mostly well characterized, and unwanted or unknown matrix constituents are therefore easier to avoid.

3.4.2. Continuous flow reactor

For larger volumes and treatment of continuously generated wastewater, flow-through reactors may be the better choice (Fig. 4B). The treatment of the wastewater is carried out during the plug-flow passage of long convoluted reactor tubes. Laboratory experiments were carried out using a coiled glass pipe (2.5 m long) as flow-through reactor. Catalyst particles and hydrogen source were fed into the contaminated water at the reactor inlet and are transported with the water flow. Pd/Fe₃O₄ nano-catalysts have the advantage of their easy and highly effective magnetic separation at the reactor outlet. After re-dispersion of the nano-particles by means of ultrasonic treatment they can be directly re-used, reactivated or substituted by fresh catalyst. In these laboratory tests, MCB was chosen as probe compound because MCB itself and its reaction product benzene are easily detectable by drawing water samples into a vial and analysing the headspace concentrations. The water retention time (or hydraulic residence time) in the coiled tubular reactor was adjusted such that an optimal particle transport was ensured and MCB conversion was incomplete ($\tau_R \approx 2$ min), in order to allow determination of the catalyst activity. The transport of the nano-catalyst through the reactor was homogeneous over the whole length of the coil.

Fig. 5 shows typical data of a reactor running for 6 h. After a few minutes a stationary conversion degree had been established that remained stable throughout the whole experiment, corresponding to a catalyst activity of $A_{Pd,MCB} = 8800 L g^{-1} min^{-1}$. This value is higher by a factor of about 2 than that measured for MCB in batch reactions ($A_{Pd} = 3700 \pm 470 L g^{-1} min^{-1}$ [13]), but nevertheless in the same order of magnitude. The recovery of the magnetite particles from the reaction suspension was carried out by means of a simple

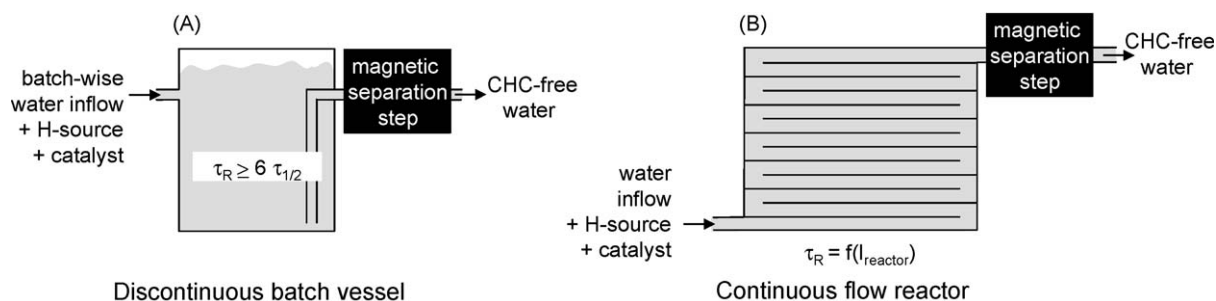


Fig. 4. Schematic presentation of two reactor concepts: (A) a tank reactor for discontinuously occurring water and (B) a tubular flow-through reactor for continuous water flow to be treated, both with a residence time of at least 6 reaction half-lives.

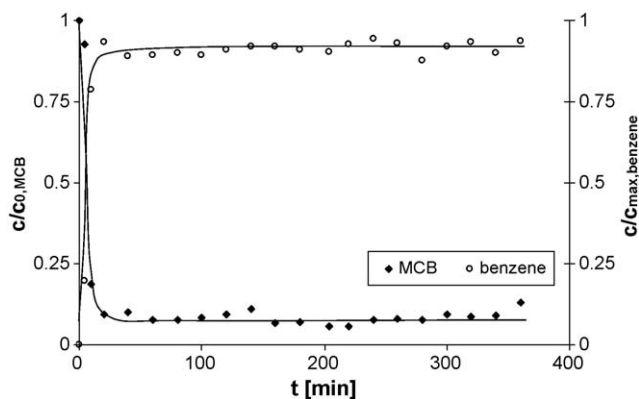


Fig. 5. Dechlorination of MCB in a continuous flow tubular reactor with continuous feed of Pd/Fe₃O₄ nano-catalyst and hydrogen ($c_{0, \text{MCB}} = 10 \text{ mg L}^{-1}$, $c_{\text{stationary, MCB}} \approx 0.85 \text{ mg L}^{-1}$, $c_{\text{Pd}} = 0.2 \text{ mg L}^{-1}$, $\tau_R = 2 \text{ min}$).

magnetic trap, consisting of a permanent magnet at the reactor outer wall with a ball of steel wool inside. A catalyst recovery of $\geq 98\%$ was achieved. The remaining 2% was deposited as a thin film of particles at the inner surface of the tubular reactor. This may partially explain the higher apparent catalyst activity under flow conditions compared with the batch experiments.

4. Conclusions

Pd/Fe₃O₄ nano-catalysts were tested for HDC reactions in the presence of various potential wastewater constituents. The catalyst proved its applicability in principle and showed an unexpectedly high resistance against common salts and solvents compared to other Pd-containing systems. Nevertheless, a number of known strong catalyst poisons must be avoided or eliminated by appropriate pre-treatments. New strategies for efficient catalyst protection are desirable and further studies are in progress.

Discontinuously operated reactor vessels as well as continuous flow-through reactors are suitable reactor types for treatment of CHC-contaminated wastewater using Pd/Fe₃O₄ nano-catalysts when connected with a magnetic separation unit. The outstanding catalyst activities, the stability of the Pd/Fe₃O₄ system in a broad pH range, and the efficient catalyst recovery by magnetic separation (and thus recyclability) are very promising preconditions for a successful application of this novel nano-catalyst system in wastewater treatment.

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